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"CHARACTERIZATION OF THE DEGREE OF OXIDATION AND FUNCTIONAL GROUPS OF A COMMERCIAL GRAPHENE"

Claudia Alejandra Castañeda-Carreño[1], Orlando Castro-Ocampo[1], Enrique Morales-Bergas[2], Edgar García-Hernández[1], Cinthya Dinorah Arrieta-González[1], René Salgado-Delgado[1], Zully Vargas-Galarza[1], Alberto Álvarez-Castillo[1*].

[1]Tecnológico Nacional de México (TecNM)/Instituto Tecnológico de Zacatepec (ITZ), División de Estudios de Posgrado e Investigación y Departamento de Ingeniería Química y Bioquímica, Calzada Tecnológico No. 27, C.P. 62780, Zacatepec de Hidalgo, Morelos. A.P. 45, México.

[2]Instituto de Ciencia y Tecnología de Polímeros (CSIC), C/ Juan de la Cierva 3, Z.C. 28006, Madrid, España.

*Corresponding author, alberto.ac@itzacatepec.edu.mx

Abstract. Graphene has been used as a reinforcing filler in polymeric nanocomposite materials due to the excellent properties it presents. Specific properties are sought to be improved in composite materials. The mechanical properties of graphene have not been successfully used in composite materials. Graphene has low compatibility with polymer matrices, and therefore, to take advantage of the mechanical properties of reinforcers. One of the strategies in the Science and Engineering of Composite Materials is to improve the compatibility of the matrix with this constituent. In the present communication, commercial graphene Avanzare with a certain degree of oxidation was analyzed by Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy and Raman Spectroscopy. The degree of oxidation was estimated from the FTIR measurements, using the quotient between the areas of bands related to oxygenated groups and the area under the curve from of C=C group. The FTIR shows the presence of carbonyl (C = O), hydroxyl (-OH), carboxyl (-COOH), aldehyde (-COH), and ketone group (-CO-), as well as evidence of intermolecular interactions. This characterization was to obtain, as a result a proposal of the matrix that will be used with this graphene to have a good fiber/matrix compatibility and in this way substantially improve the mechanical properties of the matrix.

Keywords: Polymeric Nanocomposite, Graphene, Mechanical Models.

Introduction

Carbon has different allotropic forms, being graphite and diamond the most common and known of the allotropes, since the antiquity. Graphite consists of layers of carbon atoms stacked by weak Van der Waals forces with sp^2 hybridization. The name graphene, another allotropic form, was introduced in 1994 by Boehm, Setton and Stumpp [1] and is called the carbon atoms that make up simple two-dimensional layers used to describe properties of carbon-based materials [2]. The carbon atoms in the graphene layers with their flat, hexagonal arrays are the beginning for the calculations of graphite, nanotubes and fullerenes properties that are the others allotropes of carbon. The first obtaining of graphene in 2004 by mechanical exfoliation was, led by Andre Geim and Kostya Novoselov, physicists at the University of Manchester, United Kingdom [3]. Recent publications state that graphene is of great importance because it can improve the structural, functional and mechanical properties as well as the electrical and thermal conductivities of composite polymers. Likewise, graphene has a great attention due to its excellent properties and its feasibility for engineering applications [4].

The graphene synthesis method is of crucial importance for the development of excellent mechanical properties in new materials, since depending on the obtaining method,

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graphene has different characteristics. Currently, various methods are being used to obtain graphene of various dimensions, shapes and qualities [5]. The methods can be classified into two types: top-down and bottom-up [6]. The top-down are: mechanical exfoliation [3], electrochemical exfoliation [7], chemical reduction of graphene oxide [8], obtained by three different methods (Brodie [9], Staudenmaier [10] or Hummers [11]) that involve the reaction of graphite providing several levels of oxidation.

Given its excellent mechanical properties of graphene, it has been used as a reinforcing filler in polymeric composite materials seeking to improve various properties, i.e., mechanical properties [12-15]. However, the low compatibility of graphene with polymeric matrices has generated that the mechanical properties of graphene in composites have not been efficiently exploited [16]. One of the strategies in the science and engineering of composite materials is to take advantage of the mechanical properties of the reinforcement. This only can be archived by increasing the compatibility of the matrix with this constituent [17], where the functional groups on the surface of graphene are the key to have attraction or repulsion interactive secondary in order to improvement or impoverishment this compatibility. The kind of functional groups depends on the degree of oxidation of graphene and contribute to modify their compatibility due to the polar groups generated with controlled oxidation of graphene.

In previous publications, Guerrero and Caballero [18], Viana, et al. [19], Talyzin, et al. [20] and Jeong et al. [21] characterized different samples of graphene oxide, obtaining the concentration of functional groups and the degree of oxidation. They used a combination of various methods of oxygen groups quantification (FTIR, SEM, XRD, XPS, and Raman). The degree of oxidation was estimated from the FTIR measurements, the quotient between the area of bands related to C-O group vibrations and the total area under the curve of the spectrum [18].

The surface inside the sheets influenced by their chemistry in the structure and in their optical and electrical properties of the graphene oxide powders. However any publication, up to the knowledge of the authors, has been found related to the connection between the degree of oxidation and functional groups created in the synthesis of graphene with the compatibility of the polymer matrices. Therefore, the goal of this communication is making a connection with this property and functional groups of a commercial graphene (Avanzare) with a selection of a specific polymer matrix to make composite materials to have forecasted better mechanical properties.

Methodology or experimental section

The graphene of the Avanzare Company was provided by Dr. Morales coauthor of this article and was characterized as received.

Surface morphology by scanning electron micrograph. For the study of the morphology of the graphene, a scanning electron microscope (SEM), from JEOL, model JSM-6010A, was used. A high vacuum, magnifications of 1000, 2000 and 5000x was used with a voltage of 20 kV.

Infrared spectroscopy by Fourier Transform. Fourier transform infrared spectroscopy (FTIR) analyzes were done by using the Total Attenuated Reflectance (ATR) method. A Perkin Elmer equipment was used, model SpectrumTwo. The equipment performing 16 sweeps in the mid-infrared (4,000 - 400 cm^{-1}) with a resolution of 4 cm^{-1}.

Raman spectroscopy. Raman spectra were recorded by using a Renishaw InVia Reflex Raman system, employing a grating spectrometer with a 1,200 l/mm Peltier-cooled charge-coupled device (CCD) detector, coupled to a confocal microscope. The Raman scattering was excited using a diode laser wavelength of 785 nm. The laser beam was focused on the sample with a 0.85 x 100 microscope objective, with a laser power at the sample of approximately 150 mW. The exposure and number of accumulations for the Raman measurements were 10 seconds and 5 times respectively. The spectral resolution was better than 1 cm^{-1}. All spectra were processed and fitted using Renishaw WiRE 3.3 software.

Results and discussion

Figure 1 shows the three different magnifications of commercial graphene sample.

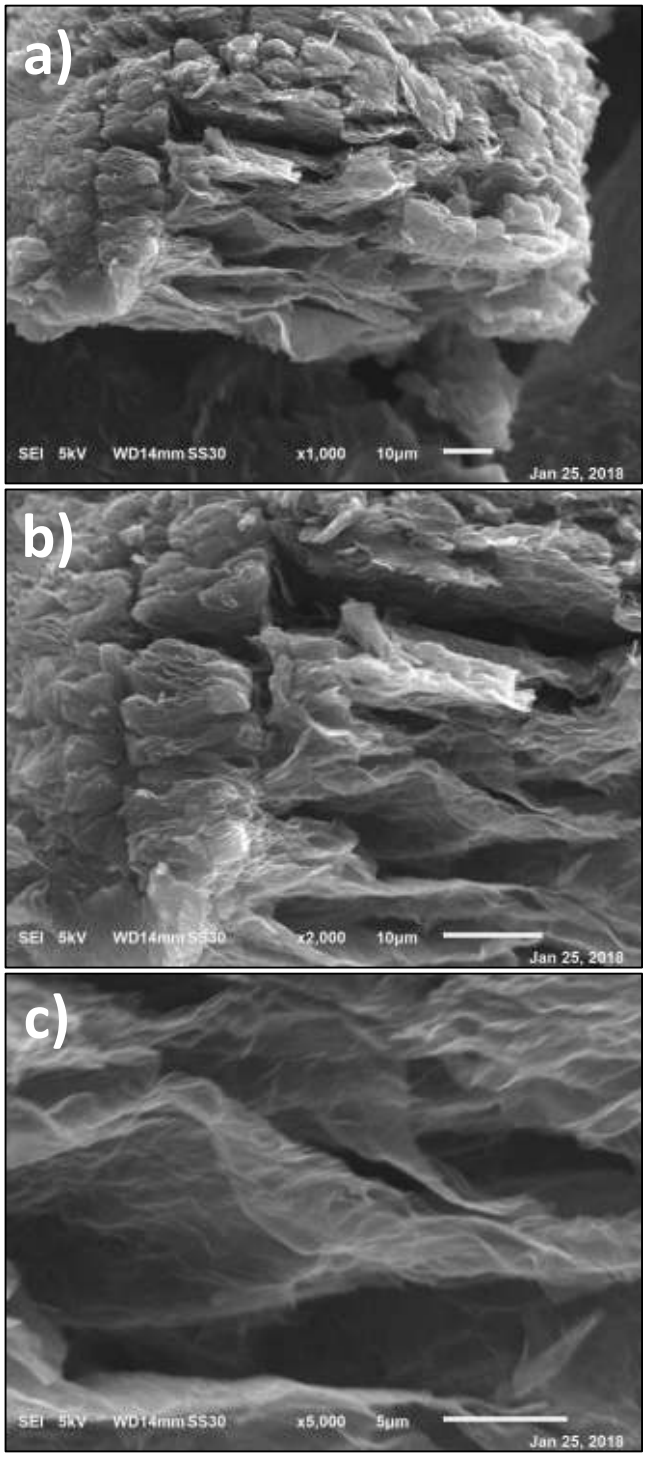

Figure 1. SEM micrographs of commercial graphene particles Avanzare powder a) 1000x, b) 2000x and c) 5000x magnification.

The sheets were observed, seeing more clearly in Figure 1c, where they have a stratified structure that produces ultra thin and homogeneous graphene films. Such films are bent or continuous depending on the order and it is possible to distinguish the edges of the individual sheets, including the folded and wrinkled areas. On the other hand, the structure suggests the intercalation of oxygen in graphene sheets. The structure are stratified by samples with low degree of oxidation and the structure of separate sheets for those with a high degree of oxidation. The thickness calculated by graphene Avanzare sheet was 0.19 µm, similar to what is reported in the literature [22]. Figure 2 shows the FTIR spectra whereas, Figure 2b shows the representative deconvoluted of the main oxygenated functional groups present in the sample. Carboxylic acid, aldehyde and ketone at 1,710 cm^{-1}, 1,730 cm^{-1} and 1,735 cm^{-1} respectively [18]. With these data, it is possible to determine the degree of oxidation relating the area under the curve of the oxygenated groups with the stretching signal of the group C = C. This signal appears at 1,475 cm^{-1} [23] and 1,548 cm^{-1} [18] representing the compound of graphene without oxidation. Table 1 lists the characteristics bands of the functional groups determined in the FTIR spectrum.

Table 1. IR frecuencies and corresponding functional groups of graphene Avanzare sample.

IR frequency (cm^{-1})	Bond and functional group	Reference
3,430	O–H bending mode	Muzyka, et al. [24].
1,710	C=O stretching vibration	Muzyka, et al. [24].
1,735	-CO- stretching vibration	Guerrero, et al. [18].
1,730	-COH stretching vibration	Guerrero, et al. [18].
1,710	-COOH- stretching vibration	Guerrero, et al. [18].
1,475	C = C stretching vibration	Cao, et al. [23].
1,548	C = C stretching vibration	Guerrero, et al. [18].

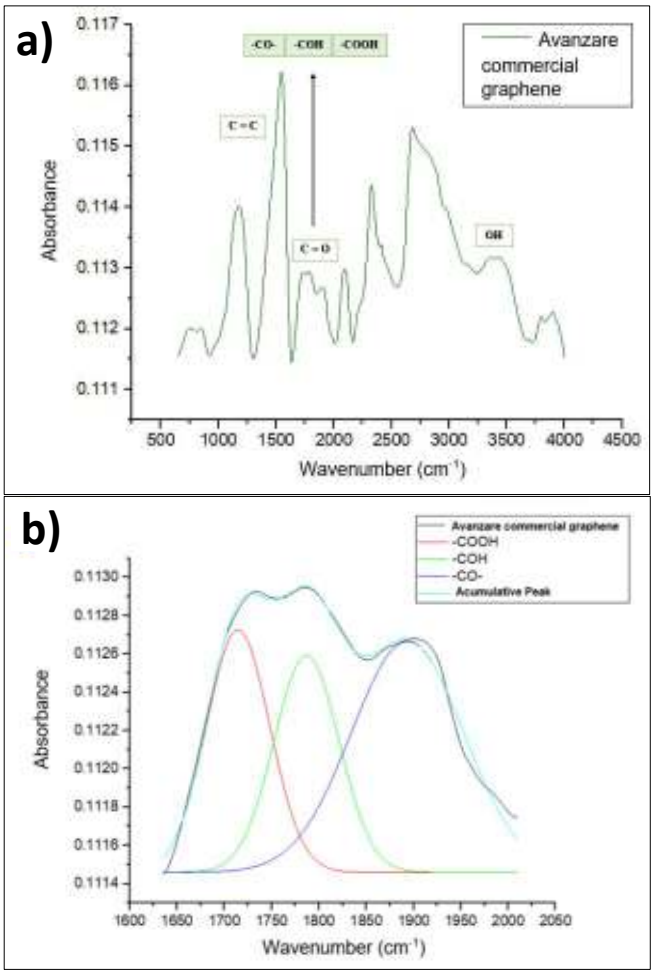

Figure 2. FTIR spectra of commercial graphene Avanzare a) total range and b) deconvolution in the range of oxygenated groups with the carbonyl group (C = O).

With data from Table 2 determined by the deconvolution of the FTIR spectrum, the degree of oxidation was determined for the commercial graphene Avanzare sample, being 0.76129. Data very similar to the literature consulted regarding the degree of oxidation of graphene oxide [18].

Table 2. Data used for the determination of degree of oxidation of the commercial graphene sample.

Functional group	Area under the curve
-COOH	0.10532
-COH	0.09769
-CO-	0.17445
C=C	0.37849
C=O	1.58561

The ketone group (-CO-) is in higher concentration, having the largest area under the curve. Therefore, it is the group that predominates among the oxygenated functional groups determined in the FTIR spectrum.

The Raman spectrum of commercial graphene Avanzare sample is shown in Figure 3, the characteristic peaks of carbon-based graphitic materials and their overtones are appreciated. The first order peaks D and G, derived from the sp^2 carbon vibrations appeared at around 1,350 cm^{-1} [1] and 1,585 cm^{-1}[25], respectively. The D band is of first order of the zone boundary phonons and the G band also provides information for the quantification of the number of layers. Its position is shifted to lower wave numbers as the thickness of the sheet increases [1]. The displacement and the shape of the overtone of peak D, called the 2D peak, appears around 2,688 cm^{-1} [22]. The 2D peak is attributed to the double resonance transitions that result in the production of two phonons with opposite impulse. A default activated peak called D+G is also easily visible near 2,925 cm^{-1} [25]. The Raman spectrum of a single graphene sheet has two characteristic features and that are appreciable in the spectrum, the G band and the G′ band. This second band refers to the aforementioned 2D band [1].

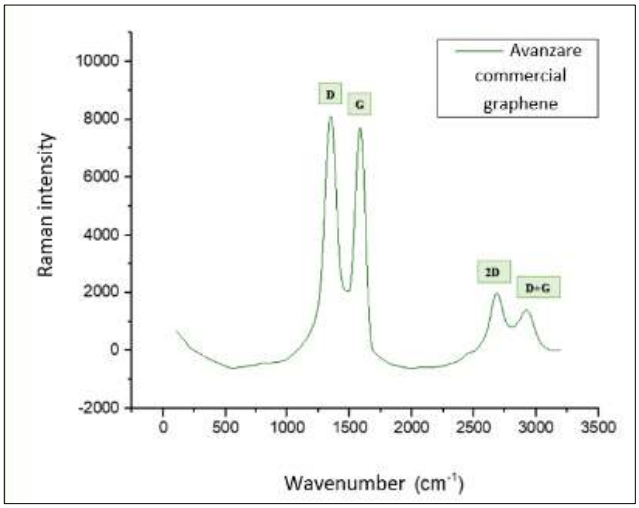

Figure 3. Raman spectrum of commercial graphene Avanzare.

Summary

Due to the qualitative and quantitative analysis obtained from the Avanzare commercial graphene, it was determined that the oxygenated functional group that predominates in the graphene sample is the ketone. Therefore, to take advantage of the mechanical properties of the reinforcers and improve the compatibility of the matrix, it is proposed to use for the analyzed sample of commercial graphene, a matrix where the functional groups on the surface thereof, are those with affinity to the addition of the ketone group to obtain, thus, a good fiber/matrix compatibility and consequently in this way improve the mechanical properties of the matrix of a composite material. Therefore poly (ether-ether ketone) [PEEK] is recommended as a matrix in the elaboration of a composite material based on this graphene, since it has benzene groups and ketonic groups, as well as the experimental evidence of functional groups of graphene of Avanzare.

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References

[1] Konstantinos Spyrou and Petra Rudolf (2014). Functionalization of Graphene. An Introduction to Graphene, First Edition. Published by Wiley-VCH Verlag GmbH & Co. KGaA. Page 1.

[2] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. (2004). Electric Field Effect in Atomically Thin Carbon Films. Science, 306 (5696): 666-669.

[3] Katsnelson, M. I. (2007). Graphene: carbon in two dimensions. Materials Today, 10 (1-2): 20-21.

[4] Ervina J.; Mariattia, M.; Hamdanb, S. (2016). Effect of Filler Loading on the Tensile Properties of Multi-walled Carbon Nanotube and Graphene Nanopowder filled Epoxy Composites. Elsevier. Procedia Chemistry 19, 897-905.

[5] Novoselov, K. S.; Fal´ko, V. I.; Colombo, L.; Gellert, P. R.; Schwab, M. G.; Kim, K.; (2012). NATURE, 490, 192-200.

[6] Narayan and Kim Nano Convergence (2015). 2:20, DOI 10.1186/s40580-015-0050-x

[7] Li, D.; Müller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. (2008). Nat Nanotech 3, 101-105.

[8] Parvez, K.; Li, R.; Punireddy, S. R.; Hernandez, Y.; Hinkel, F.;Wang, S.; Feng, X.; Mullen, K. (2013). ACS Nano 7, 3598-3606.

[9] Brodie, B. C., Ann. Chim. Phys. 1860, 59, 466.

[10] Staudenmaier, L.; Ber. Deut. Chem. Ges. 1898, 31, 1481.

[11] Hummer, W. S.; Offeman, R. E.; J. Am. Chem. Soc. 1958, 80, 1339.

[12] An, J. E.; Jeon, G. W.; Jeong, Y. G. (2012). Preparation and properties of polypropylene nanocomposites reinforced with exfoliated graphene. Fibers and Polymers, 13 (4): 507-514. https://doi.org/10.1007/s12221-012-0507-z

[13] Blanco, S. C.; Macías, E. J.; Fernández, J. B.; Pérez, M.; Parte, D.; Cámara, E. M.; Muro, J. C. S. (2015). Models for nanocomposites characterization. Summary. Nanomaterials and nanocomposites for modeling to determine mechanical properties in nanocomposites. Analytical models of rigidity.

[14] Kim, S. G.; You, N. H.; Lee, W.; Hwang, J. Y.; Kim, M. J.; Hui, D.; M. J.; Lee, J. H. (2016). Effects of the functionalized graphene

oxide on the oxygen barrier and mechanical properties of layer-by-layer assembled films. Composites Part B: Engineering, 92,307-314. https://doi.org/10.1016/j.compositesb.2016.02.028

[15] Wan, Y.-J.; Gong, L.-X.; Tang, L.-C.; Wu, L.-B.; Jiang, J. X. (2014). Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide. Composites Part A: Applied Science and Manufacturing, 64, 79-89. https://doi.org/10.1016/j.compositesa.2014.04.023

[16] Castro-Ocampo O., Morales-Bergas E., García-Hernández E., Arrieta-González C. D., Vargas-Galarza Z., Álvarez-Castillo A. (2017). Theoretical analysis vs. experimental of the mechanical properties of polymeric composite materials reinforced with graphene oxide. Electronic Journal of Research Disclosure of the SABES. 14, 1-10.

[17] Hulland, D.; Clyne, T. W. (1996). An Introduction to composite Materials, Second Edition, Cambridge University Press, Cambridge.

[18] Guerrero-Contreras, J. and Caballero-Briones F. (2015). Graphene oxide powders with different oxidation degree, prepared by synthesis variations of the Hummers method. Elsevier, 153, 209-220.

[19] Viana, M. M.; Lima, M. C. F. S.; Forsythe, J. C.; Gangoli, V. S.; Cho, M.; Cheng, Y.; Silva, GG.; Wong, M. S. and Caliman, V. (2015). Facile graphene oxide preparation by microwave-assisted acid method. J. Braz. Chem. Soc. 26(5): 978-984.

[20] Talyzin, A. V.; Mercier. G.; Klechikov, A.; Hedenstrom, M.; Johnels, D.; Wei, D.; Cotton, D.; Opitz, A.; Moons, E. (2017). Brodie vs. Hummers graphite oxides for preparation of multi-layered materials. Elsevier, 115, 430-440.

[21] Jeong, H. K.; Lee, Y. P.; Lahaye, R. J. W. E.; Park, M. H.; An, K. H.; Kim. I. J.; Yang, C. W.; Park, C. Y.; Ruoff, R. S. and Lee, Y. H. (2008). Evidence of graphitic AB stacking order of graphite oxides. JACS Articles. 40,30.

[22] Shahriary, L. and Athawale, A. A. (2014). Graphene oxide synthesized by using modified Hummers approach. International Journal of Renewable Energy and Environmental Engineering. 2(1): 58-63.

[23] Cao, N. and Zhang, Y. (2015). Study of reduced graphene oxide preparation by Hummer's method and related characterization. Journal of Nanomaterials. ID 168125, 1-5.

[24] Muzyka, R.; Kwoka, M.; Smedowski, L.; Díez, N. and Gryglewicz, G. (2017). Oxidation of graphite by different modified Hummers methods. New Carbon Materials 32(1): 15-20.

[25] Krishnamoorthy, K.; Veerapandian, M.; Yun, K. and Kim, S. J. (2013). The chemical and structural analysis of graphene oxide with different degrees of oxidation. ELSEVIER, 53, 38-49.